



HALDOR TOPSØE A/S

NYMØLLEVEJ 55 · P.O. BOX 213 · DK-2800 LYNGBY · DENMARK · CVR NO. 41853816 · VAT. NO. DK 41853816
TELEPHONE: +45 4527 2000 · FAX: +45 4527 2999 · WWW.HALDORTOPSOE.COM

24 March 2004

US404-1737003

SFC/HABS/AKN

**Method of measuring high temperatures
and instrument therefore**

BACKGROUND OF THE INVENTION

Field of the Invention

5 The invention relates to measurement of high temperatures in chemical reactors. It is specifically directed to measurement of temperatures in catalytic reactors where endothermic reactions are carried out at high temperatures. In the petrochemical industry autothermal reformers are operating under these conditions.

Description of Related Art

15 In autothermal reformers or gasifiers the process gas entering the catalyst bed is typically 1000-1500°C, and the process gas contains hydrocarbons, hydrogen, carbon monoxide, water vapour and sometimes nitrogen. Under these severe conditions the temperature is most often not measured.

20 A temperature measurement arrangement is disclosed in US patent No. 6,302,578 showing a thermowell installed in a thick reactor wall. This is done in such a way that there is a layer of hotface brick between the interior of the reactor and the tip of the thermowell with thermocouple, which thereby is protected against the high temperatures.

25 In PCT/US91/05432 another high temperature measurement is described. Here the thermocouple is protected by means of layers of ceramic insulation and a ceramic sheath.

30

However, these instruments are shielded from the reaction gasses and will not give an immediate indication of tem-

perature changes of the gases. This is especially important for temperature of gasses entering a catalyst bed in auto-thermal reformers, as this temperature is extremely sensitive to changes in flow ratio between hydrocarbon feed and oxygen source.

SUMMARY OF THE INVENTION

10 The invention provides a method for measurement of high temperatures of a process stream by means of a thermocouple arranged in a thermowell, wherein the thermowell is at least partly covered by a layer of a catalytic material being active in at least one endothermic reaction.

15 It further relates to a temperature measurement wherein the thermowell is installed in a reactor by inserting the thermowell through a hole in reactor wall so that the tip of the thermowell is in contact with the process stream.

20 It is thereby possible to let the hot gas stream contact the thermowell, as the endothermic reaction in the catalyst keeps the temperature of the metal surface of the thermowell tip considerably lower than the temperature of the gas.
25 In this way, changes in gas temperature can be instantaneously detected.

BRIEF DESCRIPTION OF THE DRAWINGS

30 FIG 1 is a cross sectional view of a temperature-measuring instrument according to a specific embodiment of the invention.

FIG 2 is a front view of FIG 1.

FIG 3 shows a typical installation of the measuring instrument shown in the above Figures.

5

DETAILED DESCRIPTION OF THE INVENTION

The invention is especially directed to temperature measurement in autothermal reformers where hydrocarbons undergo first a partial oxidation and then a reforming process.

The partial oxidation is an exothermic reaction while the reforming process is an endothermic process whereby the first reaction provides heat to the second process.

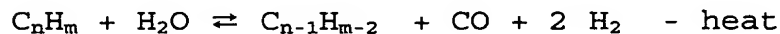
15

By the partial oxidation some of the hydrocarbons react to form carbon oxide and steam:



20

The resulting process gas then undergoes a reforming reaction:



25



The overall reforming is an endothermic reaction.

30

A hydrocarbon feed gas and an oxygen containing gas are mixed at the inlet of the reactor.

5 The hydrocarbon feed gas typically contains steam, hydrocarbon, hydrogen and carbon oxides and it is fed to the reformer at temperatures between 100 and 900°C. The oxygen source is pure oxygen, air or any mixture hereof at a temperature between ambient temperature and up to 700°C.

10 The pressure in the reactor can be 2-8 MPa, most often it is 2.5-5 MPa, and when the feed streams are mixed the exothermic oxidation process starts.

15 Although the content of oxygen corresponds to only partial combustion of the hydrocarbon the temperature rise is extremely high.

20 In the space between inlet of reactor and catalyst bed, the endothermic reforming reaction starts due to the high temperature and ends at 1000-1500°C. At steam/carbon ratios of 1.5 this reaction ends at about 1250°C and at steam/carbon ratio of 0.6 at about 1335°C.

25 The reaction continues in the catalyst bed to almost complete conversion of hydrocarbons and the temperature of the reacted, reformed process gas is typically 900-1100°C.

30 By the method of the invention the temperature of the gas entering the catalyst bed is measured by a thermocouple in a thermowell provided with a layer of catalyst being active in catalysing endothermic reactions. Although it is a relatively thin layer and the reaction may not be entirely com-

plete, the endothermic reaction will cool the surface of the thermowell considerably.

At the same time the signal from the temperature instrument of the invention is stronger than one from a measurement of prior art. This is explained below.

In case the oxygen containing feed stream to an autothermal reformer increases during normal operation, an increased amount of hydrocarbon is oxidised. This has both the consequence that the temperatures increase and that the remaining amount of hydrocarbon to be reformed decreases.

At this higher start temperature for the endothermic reaction the conversion is increased in the space without catalyst. Thereby, much less endothermic reaction takes place in the catalyst.

This means that the total temperature drop in the reactor decreases, the temperature drop in the empty space increases and the temperature drop across the catalyst decreases even more than the total decrease of temperature drop.

In this change of operation situation, a conventional temperature instrument installed just upstream of the catalyst detects a corresponding temperature increase, which is lower than the temperature increase at the inlet of the reactor. Contrary to this, a temperature instrument of the invention detects a temperature increase corresponding to catalyst outlet temperature, and this temperature increase

is even higher than the temperature increase at the inlet of the reactor.

5 The same difference in temperature change also applies, when the relative oxygen amount decreases.

10 The above illustrates that the invention has the advantages of measuring the temperature with a much lower metal surface temperature of creating a stronger signal and of measuring the gas itself inlet the catalyst bed. Measuring the catalyst outlet gas or measuring behind a shield would create a considerable time delay.

15 The temperature of the partially combusted process gas is very sensitive to the ratio between flow of hydrocarbon and flow of oxygen source.

20 Consequently, it is highly desired to detect a change in this temperature as quickly as possible. This is possible with the temperature measurement of the invention.

25 One preferred embodiment of the invention is shown on FIG 1. The measuring junction 1 of the thermocouple 2 is installed in the tip of thermowell 3, and the tip of the thermowell is covered by a catalytic layer 4. This is in contact with process gas in the reactor chamber 5. The inner surface of the reactor wall is covered by tiles 10, which are able to withstand the high reaction temperatures. The outer surface of the reactor wall is the reactor shell 30 11, which is designed for the full operation pressure. Between 10 and 11 three layers of insulating refractory material 12, 13 and 14 are installed.

The tip of the thermowell is somewhat withdrawn from the inner surface of the reactor wall to protect it against radiation from the flame at top of the reactor. The tip of the thermowell is 20-50mm from the inner surface of the wall.

As the thermal expansion of the tiles and refractory differs from the one of the metal pressure shell, to which the thermowell is connected, the height of the hole in the tiles and outer refractory layer will be bigger than the width of the hole. The dimensions are adapted to the thermal expansions, which in industrial autothermal reformers typically are a height of 80-100mm and a width of 35-40mm. This is further illustrated on FIG 2.

On the thermowell the thickness of the catalyst layer 4 is from 0.2 to 0.5mm. In another embodiment the thermowell tip is inserted into a catalyst tablet and then the "catalyst layer" is 0.5-5mm most often 0.5-2mm.

20-200mm of the end of the thermowell can be covered by the catalytic material; most often 40-80mm is covered.

The catalyst 4 can be any catalyst active in reforming reaction. Especially the catalysts with noble metals are very suitable.

FIG 3 shows where a thermowell of the invention can be installed in an autothermal reformer. The hydrocarbon feed 1 is mixed with the oxygen containing feed 2 and the partial combustion takes place in burner 3. The process gas temperature is measured by thermocouple 4, before entering

catalyst bed 5 where it is completely reformed to product gas 6.

In the industry the invention is useful in gasifiers, such as autothermal reformers producing synthesis gas in ammonia plants, hydrogen plants, methanol plants and H_2/CO gas plants. In all these reactors it is very important to thoroughly supervise their performance and especially temperatures in order to obtain a stable and safe operation.

Example

In a test pilot plant having an adiabatic reactor two experiments at autothermal reforming conditions were conducted.

In both experiments the pressure was $28 \text{ kg/cm}^2 \text{ g}$ (2.8 MPa). The hydrocarbon feed was $97.4 \text{ Nm}^3/\text{h}$ natural gas with $2 \text{ Nm}^3/\text{h}$ hydrogen at 562°C .

Steam/carbon ratio was 0.38 (on molar basis).

The oxygen was fed at 219°C .

Two thermocouples TI-1 and TI-2 were installed measuring the gas entering the catalyst bed.

TI-3 measured the gas exit the catalyst bed.

Following results were obtained:

Measured data	1 st experi- ment	2 nd experi- ment
O ₂ /natural gas, by volume	0.519	0.576
TI-1, °C	1163	1201
TI-2, °C	1184	1221
TI-3, °C	991	1068
Calculated data		
T, inlet, average	1174	1211
ΔT , inlet-exit	183	143
Increase of T, inlet, average from 1 st to 2 nd experi- ment	37	
Increase of T, outlet from 1 st to 2 nd experi- ment	77	

- 5 This demonstrates that when the oxygen content increases, the reaction and the temperature drop decreases in the catalyst bed. Also, the increase from experiment 1 to 2 of catalyst inlet temperature is less than the increase of catalyst outlet temperature. From this it appears that a

catalyst coated thermowell installed thermocouple gives a stronger signal and with a lower metal surface temperature.